

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 June 2002 (13.06.2002)

PCT

(10) International Publication Number
WO 02/46517 A1

- (51) International Patent Classification⁷: **D06L 1/04**
- (21) International Application Number: PCT/US01/26918
- (22) International Filing Date: 28 August 2001 (28.08.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/730,816 6 December 2000 (06.12.2000) US
- (71) Applicant: **GENERAL ELECTRIC COMPANY**
[US/US]; 1 River Road, Schenectady, NY 12345 (US).
- (72) Inventors: **PERRY, Robert, J.**; 2115 Niskayuna Drive,
Niskayuna, NY 12309 (US). **RICCIO, Donna, Ann**; 138
Haswell Road, Watervliet, NY 12189 (US). **RYAN, Larry,**
D.; 18 Birch Glen Drive, Waterford, NY 12188 (US).
- (74) Agents: **HARRINGTON, Mark, F.**; Harrington & Smith,
LLP, 1809 Black Rock Turnpike, Fairfield, CT 06432-3504
et al. (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK,
SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,
TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: SILOXANE DRY CLEANING COMPOSITION AND PROCESS

(57) Abstract: A dry cleaning composition comprising a volatile siloxane and an organic surfactant and, optionally water, and a method for dry cleaning comprising contacting an article with a composition comprising a volatile siloxane and an organic surfactant.

WO 02/46517 A1

SILOXANE DRY CLEANING COMPOSITION AND PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims rights of priority from U.S. Provisional Patent Application Serial No. 60/184,108, filed February 22, 2000.

TECHNICAL FIELD

The present invention is directed to a dry cleaning composition, more specifically, to a siloxane fluid based composition, for use in dry cleaning and to a dry cleaning process using the composition.

BACKGROUND

Current dry cleaning technology uses perchloroethylene ("PERC") or
5 petroleum-based materials as the cleaning solvent. PERC suffers from toxicity and odor issues. The petroleum-based products are not as effective as PERC in cleaning garments.

Cyclic siloxanes have been reported as spot cleaning solutions, see US
4,685,930, and as dry cleaning fluids in dry cleaning machines, see US
10 5,942,007. Other patents disclose the use of silicone soaps in petroleum solvents, see JP 09299687, and the use of silicone surfactants in super critical carbon dioxide solutions has been reported, see, for example, US 5,676,705 and Chem. Mark. Rep., 15 Dec 1997, 252(24), p. 15. Non-volatile silicone oils have also been used as the cleaning solvent requiring removal by a second
15 washing with perfluoroalkane to remove the silicone oil, see JP 06327888.

Numerous other patents have issued in which siloxanes or organomodified silicones have been present as addenda in PERC or petroleum based dry cleaning solvents, see, for example, WO 9401510; US 4911853; US 4005231; US 4065258.

There is a continued interest in providing an additive or additives to enhance the cleaning ability of silicone based dry cleaning solvents.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a dry cleaning composition, comprising a volatile cyclic, linear or branched siloxane and one
5 or more organic surfactants.

In a second aspect, the present invention is directed to a method for dry cleaning an article, comprising contacting the article with a composition comprising a cyclic, linear or branched siloxane and an organic surfactant which may be chosen from the classes of nonionic, cationic, anionic or
10 amphoteric.

The process of the present invention exhibits improved performance, such as for example, removal of water soluble stains from the article, for example a garment, being cleaned. The process of the present invention also effectively removes most soluble stains, including oil stains and grease stains.

DETAILED DESCRIPTION OF THE INVENTION

15 In a preferred embodiment, the composition comprises, based on 100 parts by weight ("pbw") of the composition, from greater than 90 pbw to 99.99 pbw, more preferably from 92 pbw to 99.9 pbw and even more preferably from 95 pbw to 99.5 pbw of the siloxane and from 0.001 pbw to less than 10 pbw, more preferably from 0.01 pbw to 8 pbw and even more
20 preferably from 0.1 pbw to 5 pbw of the surfactant. The composition optionally further comprises water, preferably from 0.01 pbw to 15 pbw, more preferably from 0.1 pbw to less than 12 pbw and even more preferably from 0.2 pbw to 10 pbw of water. Preferably, the composition does not include siloxane resins or crosslinking agents.

In a preferred embodiment, the water may be added as "free" water or may be delivered by an emulsion containing other components such as siloxanes, hydrocarbons, surfactants, or other suitable additives. If the water is delivered by an emulsion, the emulsion may be prepared by either
 5 homogenization of the components or by mechanically stirring the mixture.

Compounds suitable as the linear or branched, volatile siloxane solvent of the present invention are those containing a polysiloxane structure that includes from 2 to 20 silicon atoms. Preferably, the linear or branched, volatile siloxanes are relatively volatile materials, having, for example, a
 10 boiling of below about 300°C point at a pressure of 760 millimeters of mercury ("mm Hg").

In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more compounds of the structural formula (I):



15 wherein:

M is $R^1_3SiO_{1/2}$;

D is $R^2R^3SiO_{2/2}$;

T is $R^4SiO_{3/2}$;

and Q is $SiO_{4/2}$

20 R^1 , R^2 , R^3 and R^4 are each independently a monovalent hydrocarbon radical; and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq 10$.

Suitable monovalent hydrocarbon groups include acyclic hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals, monovalent and

aromatic or fluoro containing hydrocarbon radicals. Preferred monovalent hydrocarbon radicals are monovalent alkyl radicals, monovalent aryl radicals and monovalent aralkyl radicals.

As used herein, the term "(C₁-C₆)alkyl" means a linear or branched alkyl group containing from 1 to 6 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl.

As used herein, the term "aryl" means a monovalent unsaturated hydrocarbon ring system containing one or more aromatic or fluoro containing rings per group, which may optionally be substituted on the one or more aromatic or fluoro containing rings, preferably with one or more (C₁-C₆)alkyl groups and which, in the case of two or more rings, may be fused rings, including, for example, phenyl, 2,4,6-trimethylphenyl, 2-isopropylmethylphenyl, 1-pentalenyl, naphthyl, anthryl, preferably phenyl.

As used herein, the term "aralkyl" means an aryl derivative of an alkyl group, preferably a (C₂-C₆)alkyl group, wherein the alkyl portion of the aryl derivative may, optionally, be interrupted by an oxygen atom, such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenoxypropyl, biphenyloxypropyl.

In a preferred embodiment, the monovalent hydrocarbon radical is a monovalent (C₁-C₆)alkyl radical, most preferably, methyl.

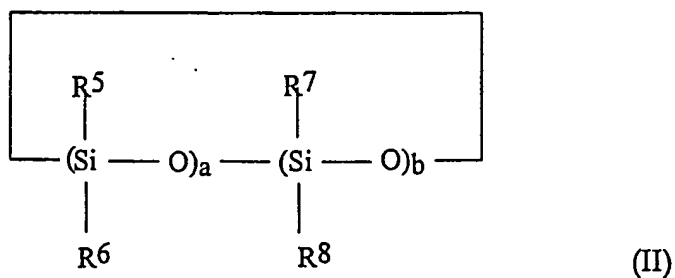
In a preferred embodiment, the linear or branched, volatile siloxane comprises one or more of, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane or hexadecamethylheptasiloxane or methyltris(trimethylsiloxy)silane. In a more highly preferred embodiment, the linear or branched, volatile siloxane of the present invention comprises

octamethyltrisiloxane, decamethyltetrasiloxane, or dodecamethylpentasiloxane or methyltris(trimethylsiloxy)silane. In a highly preferred embodiment, the siloxane component of the composition of the present invention consists essentially of decamethyltetrasiloxane.

5 Suitable linear or branched volatile siloxanes are made by known methods, such as, for example, hydrolysis and condensation of one or more of tetrachlorosilane, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, or by isolation of the desired fraction of an equilibrate mixture of hexamethyldisiloxane and octamethylcyclotetrasiloxane or the like
10 and are commercially available.

 Compounds suitable as the cyclic siloxane component of the present invention are those containing a polysiloxane ring structure that includes from 2 to 20 silicon atoms in the ring. Preferably, the linear, volatile siloxanes and cyclic siloxanes are relatively volatile materials, having, for example, a
15 boiling point of below about 300°C at a pressure of 760 millimeters of mercury ("mm Hg").

 In a preferred embodiment, the cyclic siloxane component comprises one or more compounds of the structural formula (II):



20 wherein:

R⁵, R⁶, R⁷ and R⁸ are each independently a monovalent hydrocarbon group;
and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq (a + b) \leq 10$.

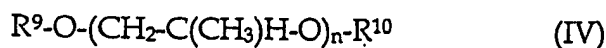
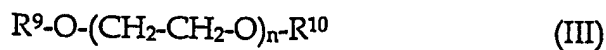
In a preferred embodiment, the cyclic siloxane comprises one or more of, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane,
5 dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane. In a more highly preferred embodiment, the cyclic siloxane of the present invention comprises octamethylcyclotetrasiloxane or decamethylcyclopentasiloxane. In a highly preferred embodiment, the cyclic
10 siloxane component of the composition of the present invention consists essentially of decamethylcyclopentasiloxane.

Suitable cyclic siloxanes are made by known methods, such as, for example, hydrolysis and condensation of dimethyldichlorosilane and are commercially available.

The organic surfactant of the present invention comprises one or more
15 surfactants selected from nonionic, cationic, anionic and amphoteric surfactants. In another embodiment, the organic surfactant comprises a mixture of two or more surfactants of the same or different classes, as long as they are compatible, such as, for example, a mixture of two or more nonionic, cationic, anionic or amphoteric surfactants, a mixture of nonionic and cationic
20 surfactants, a mixture of nonionic and anionic surfactants, a mixture of nonionic and amphoteric surfactants, a mixture of cationic and anionic surfactants, a mixture of cationic and amphoteric surfactants, a mixture of anionic and amphoteric surfactants, a mixture of nonionic, cationic and anionic surfactants, a mixture of nonionic, anionic and amphoteric
25 surfactants, a mixture of cationic anionic and amphoteric surfactants, or a mixture of nonionic, cationic, anionic and amphoteric surfactants.

Compounds suitable for use as the nonionic surfactant of the present invention are those that carry no discrete charge when dissolved in aqueous media. Nonionic surfactants are generally known in the art and include, for example, alkanol amides (such as, for example, coco, lauric, oleic and stearic monoethanolamides, diethanolamides and monoisopropanolamides), amine oxides (such as, for example, polyoxyethylene ethanolamides and polyoxyethylene propanolamides), polyalkylene oxide block copolymers (such as, for example, poly(oxyethylene-co-oxypropylene)), ethoxylated alcohols, (such as, for example, isostearyl polyoxyethylene alcohol, lauryl, cetyl, stearyl, oleyl, tridecyl, trimethylnonyl, isodecyl, tridecyl), ethoxylated alkylphenols (such as, for example, nonylphenol), ethoxylated amines and ethoxylated amides, ethoxylated fatty acids, ethoxylated fatty esters and ethoxylated fatty oils (such as, for example, mono- and diesters of acids such as lauric, isostearic, pelargonic, oleic, coco, stearic, and ricinoleic, and oils such as castor oil and tall oil), fatty esters, fluorocarbon containing materials, glycerol esters (such as, for example, glycerol monostearate, glycerol monolaurate, glycerol dilaurate, glycerol monoricinoleate, and glycerol oleate), glycol esters (such as, for example, propylene glycol monostearate, ethylene glycol monostearate, ethylene glycol distearate, diethylene glycol monolaurate, diethylene glycol monolaurate, diethylene glycol monooleate, and diethylene glycol stearate), lanolin-based surfactants, monoglycerides, phosphate esters, polysaccharide ethers, propoxylated fatty acids, propoxylated alcohols, and propoxylated alkylphenols, protein-based organic surfactants, sorbitan-based surfactants (such as, for example, sorbitan oleate, sorbitan monolaurate, and sorbitan palmitate), sucrose esters and glucose esters, and thio- and mercapto-based surfactants.

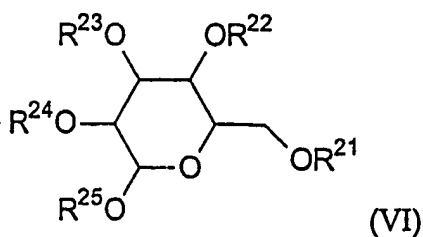
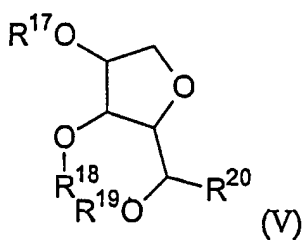
In a preferred embodiment, one component of the present invention comprises one or more nonionic surfactants according to one or more of the structural formulas III and IV:



wherein:

R^9 is a monovalent hydrocarbon group of 1-30 carbons that may be linear, cyclic, branched, unsaturated, aromatic or fluoro containing, R^{10} is hydrogen or a monovalent hydrocarbon group of 1 to 30 carbons that may be linear, cyclic, branched, unsaturated, aromatic or fluoro containing, and n is from about 1 to about 100, more preferably from about 1 to about 40. In a highly preferred embodiment, R^9 contains from 2 to about 24 carbons, even more preferably from 8 to 24 carbons, R^{10} is H and n is from about 2 to about 20.

In another preferred embodiment, one component of the present invention comprises one or more nonionic surfactants that may be a sugar-based surfactant according to one or more of the structural formulas V and VI:

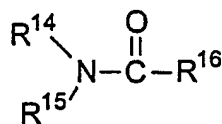


wherein:

each R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴ and R²⁵ is independently H or a monovalent hydrocarbon group of 1 to 30 carbons that may be linear, cyclic, branched, an oxygenated alkane or other chalcogen containing group.

5 Chalcogens are herein specifically defined as oxygen, sulfur, selenium, tellurium and polonium. These surfactants may also be the open-chain analogs. In a preferred embodiment, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴ and R²⁵ are each H or a hydrocarbon group of 1 to 24 carbons, preferably a polyether or ester, even more preferably, one of R¹⁷ and R²⁰ is a hydrocarbon of from 8
10 to 24 carbons while the other is H or a hydrocarbon of from 1 to 4 carbons, such as -CH₂OH or -CH₂CH₃, and one of R²¹ and R²⁵ is H or a hydrocarbon of from 8 to 24 carbons while the other is a hydrocarbon of from 1 to 4 carbons, such as -CH₂OH or -CH₂CH₃. In another preferred embodiment, the surfactant or surfactants are chosen from sucrose esters, glucose esters,
15 monoglycerides, polysaccharide ethers and sorbitan-based surfactants.

In another preferred embodiment, one component of the present invention comprises one or more nonionic surfactants that may be an amine-based or phosphate ester-based surfactant according to one or more of the structural formulas VII and VIII:



(VII)

(VIII)

wherein:

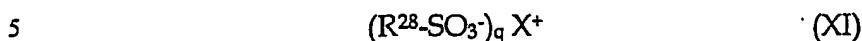
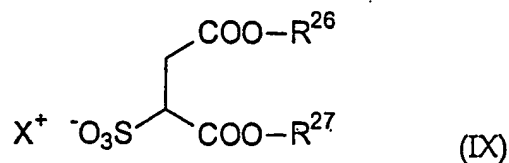
each R¹¹, R¹², R¹³, R¹⁴, R¹⁵, and R¹⁶ is independently H or a monovalent hydrocarbon group of 1 to 30 carbons that may be linear, cyclic, branched,
25 unsaturated, aromatic, fluoro containing, an oxygenated alkane or other

chalcogen containing group. In a preferred embodiment, two of R^{11} , R^{12} and R^{13} , are H or hydrocarbon groups of 1 to 4 carbons, and one is a hydrocarbon group of from 8 to 24 carbons, and R^{14} and R^{15} are either H or hydrocarbon groups of from 1 to 4 carbons while R^{16} is a hydrocarbon group of from 8 to 24 carbons, or R^{14} and R^{15} are hydrocarbon groups of from 8 to 24 carbons while R^{16} is a hydrocarbon group of from 1 to 4 carbons. In a most preferred embodiment, the surfactant or surfactants are chosen from alkanol amides, amine oxides, ethoxylated amines, ethoxylated amides and phosphate esters.

Compounds suitable for use as the anionic surfactant of the present invention are those having polar, solubilizing groups such as carboxylate, sulfonate, sulfate and phosphate. Anionic surfactants are generally known in the art and include, for example, alkyl aryl sulfonates (such as, for example, alkylbenzenesulfonates), alkyl aryl sulfonic acids (such as, for example, sodium and ammonium salts of toluene-, xylene- and isopropylbenzenesulfonic acids), sulfonated amines and sulfonated amides (such as, for example, amidosulfonates), carboxylated alcohols and carboxylated alkylphenol ethoxylates, diphenyl sulfonates, fatty esters, isethionates, lignin-based surfactants, olefin sulfonates (such as, for example, $RCH=CHSO_3Na$, where R is $C_{10}-C_{16}$), phosphorous-based surfactants, protein based surfactants, sarcosine-based surfactants (such as, for example, N-acylsarcosinates such as sodium N-lauroylsarcosinate), sulfates and sulfonates of oils and/or fatty acids, sulfates and sulfonates of ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfates of aromatic or fluoro containing compounds, sulfosuccinamates, sulfosuccinates (such as, for example, diamyl-, dioctyl- and diisobutylsulfosuccinates), taurates, and sulfonic acids.

In a preferred embodiment, one component of the present invention comprises one or more anionic surfactants that may be a sulfosuccinate,

sulfate, sulfonate, carboxylate, or phosphorous containing surfactant according to one or more of the structural formulas IX to XIII:



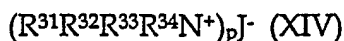
wherein:

each R^{26} , R^{27} , R^{28} , R^{29} and R^{30} is independently a monovalent hydrocarbon group of 1 to 30 carbons that may be linear, cyclic, branched, unsaturated, aromatic, fluoro containing, an oxygenated alkane or other chalcogen containing radical, and X is H or an alkali metal, alkaline earth element or a chalcogen containing counterion or other suitable cation that does not unduly interfere with the functioning of the molecule as a surfactant where the subscript q is the valence or oxidation state of the cation X. In a preferred embodiment, R^{26} and R^{27} are linear hydrocarbon groups of from 4 to 20 carbons, more preferably 6 to 13 carbons, R^{28} is a hydrocarbon group of from 6 to 20 carbons, more preferably from 8 to 16 carbons, and R^{29} is a hydrocarbon group of from 8 to 26 carbons, more preferably from 10 to 20 carbons, and R^{30} is a hydrocarbon of from 8 to 30 carbons.

Compounds suitable for use as the cationic surfactant of the present invention are those having a positive charge when dissolved in aqueous media, which resides on an amino or quaternary nitrogen. Cationic

surfactants are generally known in the art and include, for example, amine acetates, amines (such as, for example, oxygen-free amines such as monoalkylamines, dialkylamines and N-alkyltrimethylene diamines, and oxygen-containing amines such as amine oxides, ethoxylated alkylamines, 1-
5 (2-hydroxyethyl)-2-imidazolines, and alkoxyates of ethylenediamine), and quaternary ammonium salts (such as, for example, dialkyldimethylammonium salts, alkylbenzyldimethylammonium chlorides, alkyltrimethylammonium salts and alkylpyridium halides), and quaternary ammonium esters (such as, for example, diethyl ester dimethyl ammonium
10 chloride).

In a preferred embodiment, one component of the present invention comprises one or more cationic surfactants that may be a quaternary amine-based surfactant according to the structural formula XIV:



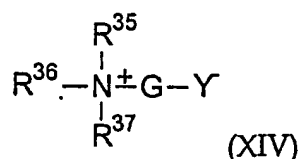
15 wherein:

each R^{31} , R^{32} , R^{33} , and R^{34} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons that may be linear, cyclic, branched, unsaturated, aromatic, fluoro containing, an oxygenated alkane or other chalcogen containing group, and J is a suitable anion having an oxidation state or
20 valence p that does not unduly interfere with the functioning of the molecule as a surfactant. In a preferred embodiment, R^{31} and R^{32} are hydrocarbon groups of from 1 to 4 carbons, more preferably, methyl, and R^{33} and R^{34} are hydrocarbon groups of from 6 to 30 carbons, more preferably from 8 to 24 carbons.

25 Compounds suitable for use as the amphoteric surfactant of the present invention are those containing both an acidic and basic hydrophilic group. Amphoteric surfactants are compatible with anionic and cationic surfactants.

Amphoteric surfactants are generally known in the art and include, for example, betaine derivatives such as alkylbetaines and amidopropylbetaines, block copolymers, imidazolines and lecithins.

In a preferred embodiment, one component of the present invention comprises one or more amphoteric surfactants according to the structural formula XV:



wherein:

each R^{35} , R^{36} and R^{37} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons that may be linear, cyclic, branched, unsaturated, aromatic, fluoro containing, an oxygenated alkane or other chalcogen containing group, G is a divalent spacer group, and Y is a carboxylate, sulfonate, sulfate, phosphonate or other similar group. In a preferred embodiment, R^{35} , is a hydrocarbon of from 1 to 4 carbons, and R^{36} and R^{37} are hydrocarbons of from 6 to 24 carbons.

Surfactants are known in the art and are commercially available under many trade names from many sources, such as for example, Akzo Chemical Co., Calgene Chemical Inc., Emkay Chemical Co, Hercules, Inc., ICI Americas Inc., Lonza, Inc., Rhone Poulenc, Inc., Union Carbide Corp. and Witco Corp.

In a preferred embodiment, the dry cleaning composition of the present invention further comprises a minor amount, preferably, less than 50 pbw per 100 pbw of the composition, more preferably, less than 10 pbw per 100 pbw of the composition, of one or more non-siloxane fluids. Suitable non-siloxane fluids include aqueous fluids, such as, for example, water, and

organic fluids, for example, hydrocarbon fluids and halogenated hydrocarbon fluids.

5 An article, such as for example, a textile or leather article, typically, a garment, is dry cleaned by contacting the article with the composition of the present invention. In a preferred embodiment, the articles to be cleaned include textiles made from natural fibers, such as for example, cotton, wool, linen and hemp, from synthetic fibers, such as, for example, polyester fibers, polyamide fibers, polypropylene fibers and elastomeric fibers, from blends of natural and synthetic fibers, from natural or synthetic leather or natural or
10 synthetic fur.

The article and dry cleaning composition are then separated, by, for example, one or more of draining and centrifugation. In a preferred embodiment, separation of the article and dry cleaning composition is followed by the application of heat, preferably, heating to a temperature of
15 from 15°C to 120°C, preferably from 20°C to 100°C, or reduced pressure, preferably, a pressure of from 1 mm Hg to 750 mm Hg, or by application of both heat and reduced pressure, to the article.

Testing for water soluble stain removal was accomplished using fabric swatches supplied by the International Fabricare Institute ("IFI") (Silver
20 Spring, MD) that contained a water soluble dye. The color change of a swatch of this material was measured by a Minolta CR-300® Colorimeter using the Hunter Color Number difference calculations. The larger the change in Hunter Color Number (ΔE), the greater the dye removal and the more efficient the cleaning.

25 The following examples are to illustrate the invention and are not to be construed as limiting the claims.

EXAMPLES

Testing procedure: Circular swatches (from IFI) containing a water soluble dye were measured by the colorimeter, and the initial color values for L, a and b (as defined by the Hunter Color Numbers) were recorded. The fabric swatches were then placed in vials containing the cleaning composition of the present invention, and the vial was shaken for 10 minutes at ambient temperature. The fabric swatch was removed and allowed to drip dry for 2 to 5 seconds, then placed on absorbent toweling and allowed to air dry for 16 to 24 hours. A second reading of each fabric swatch was taken and the color difference (ΔE) was determined using the following formula:

$$\Delta E = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2}$$

This color difference represents the relative amount of cleaning, with the higher ΔE indicative of better cleaning performance.

Example 1 - Nonionic surfactants [ethoxylated alcohols]

A cleaning composition according to the present invention containing a cyclic siloxane (D_5) and one or more nonionic surfactants was made. Fabric swatches were cleaned using the above procedure, and the color difference was measured to determine the effectiveness of the cleaning composition. A solution of cyclic siloxane (D_5) without a surfactant was used as a control.

Nonionic surfactants used in the example are those represented by formula III above, where R^9 and n are as described in Table 1, and R^{10} is H.

Table 1 - Ethoxylated Alcohols

| Exp. No. | R ⁹ | n | pbw | ΔE |
|-----------|-------------------------------------|-------|-----------|-------------|
| 1 | C ₄ | 1 | 1 | 1.9 |
| 2 | C ₄ | 1 | 5 | 2.7 |
| 3 | C ₄ | 2 | 1 | 3.2 |
| 4 | C ₄ | 2 | 5 | 3.2 |
| 5 | C ₁₂₋₁₅ | 3 | 1 | 38.8 |
| 6 | C ₁₂₋₁₅ | 3 | 5 | 41.1 |
| 7 | C ₁₂₋₁₃ | 9 | 1 | 37.8 |
| 8 | C ₁₂₋₁₃ | 9 | 5 | 38.7 |
| 9 | C ₁₂₋₁₃ | 6.5 | 1 | 39.1 |
| 10 | C ₁₂₋₁₃ | 6.5 | 5 | 38.7 |
| 11 | C ₁₄₋₁₅ | 7 | 1 | 2.0 [18.7] |
| 12 | C ₁₄₋₁₅ | 7 | 5 | 39.0 [33.7] |
| 13 | C ₁₂₋₁₃ / C ₄ | 6.5/1 | 5 (50/50) | 41.5 |
| 14 | C ₁₂₋₁₃ / C ₄ | 9/1 | 5 (50/50) | 42.9 |
| 15 | C ₁₂₋₁₅ / C ₄ | 3/1 | 5 (50/50) | 13.8 |
| 16 | C ₁₄₋₁₅ / C ₄ | 7/1 | 5 (50/50) | 41.1 |
| 17 | C ₁₂ | 4 | 1 | 35.8 |
| 18 | C ₁₂ | 4 | 5 | 40.7 |
| 19 | C ₁₂ | 23 | 1 | 0.9 |
| 20 | C ₁₂ | 23 | 5 | 1.3 |
| 21 | C ₁₆ | 2 | 1 | 4.6 |
| 22 | C ₁₆ | 2 | 5 | 2.0 |
| 23 | C ₁₈ | 2 | 1 | 2.6 |
| 24 | C ₁₈ | 2 | 5 | 19.0 |
| 25 | C ₁₈ | 10 | 1 | 2.4 |
| 26 | C ₁₈ | 10 | 5 | 23.4 |
| 27 | C ₁₈ | 20 | 1 | 4.0 |
| 28 | C ₁₈ | 20 | 5 | 22.8 |
| 29 | C ₁₂ / C ₄ | 4 /1 | 5 (50/50) | 41.1 |
| 39 | C ₁₂ / C ₄ | 23/1 | 5 (50/50) | 1.6 |
| 31 | C ₁₆ / C ₄ | 2/1 | 5 (50/50) | 3.7 |
| 32 | C ₁₈ / C ₄ | 2/1 | 5 (50/50) | 11.4 |
| 33 | C ₁₈ / C ₄ | 10/1 | 5 (50/50) | 21.1 |
| 34 | C ₁₈ / C ₄ | 20/1 | 5 (50/50) | 34.4 |
| Control 1 | -- | -- | 0 | 1.9 |

Table 1 shows that nonionic surfactants enhance the cleaning and dye removal of the base cyclic siloxane (D₅) solvent.

Example 2 - Anionic Surfactants

A cleaning composition according to the present invention containing a cyclic siloxane (D₅) and one or more anionic surfactants was made. Fabric swatches were cleaned using the above procedure, and the color difference was measured to determine the effectiveness of the cleaning composition. A solution of cyclic siloxane (D₅) without a surfactant was used as a control.

Table 2 - Sulfosuccinates

| Exp. | Designation* | mixture | pbw | ΔE |
|-----------|----------------|---------|-----|------|
| 35 | Aerosol TR | -- | 1 | 2.8 |
| 36 | Aerosol TR | -- | 5 | 6.5 |
| 37 | Aerosol OT | -- | 1 | 1.6 |
| 38 | Aerosol OT | -- | 5 | 2.3 |
| 39 | Aerosol GPG | -- | 1 | 3.0 |
| 40 | Aerosol GPG | -- | 5 | 3.0 |
| 41 | Aerosol TR/OT | 50/50 | 1 | 1.5 |
| 42 | Aerosol TR/OT | 50/50 | 5 | 2.5 |
| 43 | Aerosol TR/GPG | 50/50 | 1 | 6.9 |
| 44 | Aerosol TR/GPG | 50/50 | 5 | 16.9 |
| 45 | Aerosol OT/GPG | 50/50 | 1 | 4.6 |
| 46 | Aerosol OT/GPG | 50/50 | 5 | 6.7 |
| Control 2 | -- | -- | 0 | 1.9 |

*Commercially available from Cytek Industries

Table 2 shows that the anionic sulfosuccinate surfactants enhanced the water soluble dye removal of the base cyclic siloxane (D₅) solvent. (Surfactant TR is a solution in 20% ethanol and 10% water; GPG is a solution in 8% ethanol and 22% water.)

Example 3 - Cationic and Anionic Surfactants

A cleaning composition according to the present invention containing a cyclic siloxane (D₅) and one or more anionic and cationic surfactants was made. Fabric swatches were cleaned using the above procedure, and the color

difference was measured to determine the effectiveness of the cleaning composition. A solution of cyclic siloxane (D₅) without a surfactant was used as a control.

Table 3 - Ionic Surfactants (Cationic and Anionic)

| Exp | Type | R | pbw | ΔE |
|-----------|--|------------------------------|-----|------|
| 47 | R-SO ₄ -Na ⁺ | C ₁₄₋₁₆ alkene | 5 | 11.2 |
| 48 | R ₂ Me ₂ N ⁺ Cl ⁻ | C ₁₂ | 1 | 41.5 |
| 49 | R ₂ Me ₂ N ⁺ Cl ⁻ | C ₁₂ | 5 | 41.2 |
| 50 | DDBSA | -- | 1 | 51.5 |
| 51 | DDBSA | -- | 5 | 50.4 |
| 52 | R-PhO-(EO) ₃ - OSO ₃ -Na ⁺ | C ₁₂ | 1 | 6.2 |
| 53 | R-PhO-(EO) ₃ - OSO ₃ -Na ⁺ | C ₁₂ | 5 | 5.3 |
| 54 | R-SO ₄ -Na ⁺ | C ₁₂ | 1 | 2.7 |
| 55 | R-SO ₄ -Na ⁺ | C ₁₂ | 5 | 3.4 |
| Control 3 | -- | -- | 0 | 1.9 |

5 Table 3 shows that the ionic surfactants enhanced the water soluble dye removal of the base cyclic siloxane (D₅) solvent. (R₂Me₂N⁺Cl⁻ came as a solution in water.)

Example 4 - Nonionic surfactants with water

10 A cleaning composition according to the present invention containing a cyclic siloxane (D₅), water and a nonionic surfactant was made. Fabric swatches were cleaned using the above procedure, and the color difference was measured to determine the effectiveness of the cleaning composition. A solution of cyclic siloxane (D₅) without a surfactant was used as a control. Nonionic surfactants used in the example are those represented by formula III above, where R⁹ and n are as described in Table 4, and R¹⁰ is H.

Table 4 - Nonionic Surfactants

| Exp. No. | R ⁹ | n | pbw solvent | pbw surfactant | pbw water | ΔE |
|-----------|--------------------|-----|-------------|----------------|-----------|------------|
| 1 | C ₁₂₋₁₃ | 6.5 | 95 | 4 | 1 | 39.5 |
| 2 | C ₁₂₋₁₃ | 6.5 | 95 | 1 | 4 | 33.1 |
| 3 | C ₁₂₋₁₃ | 6.5 | 98 | 1 | 1 | 13.8 |
| 4 | C ₁₂₋₁₃ | 9 | 95 | 4 | 1 | 34.9 |
| 5 | C ₁₂₋₁₃ | 9 | 95 | 1 | 4 | 38.3 |
| 6 | C ₁₂₋₁₃ | 9 | 98 | 1 | 1 | 25.5 |
| 7 | C ₁₂₋₁₅ | 3 | 95 | 4 | 1 | 7.7 |
| 8 | C ₁₂₋₁₅ | 3 | 95 | 1 | 4 | 38.3 |
| 9 | C ₁₂₋₁₅ | 3 | 98 | 1 | 1 | 38.9 |
| 10 | C ₁₄₋₁₅ | 7 | 95 | 4 | 1 | 34.5 |
| 11 | C ₁₄₋₁₅ | 7 | 95 | 1 | 4 | 36.4 |
| 12 | C ₁₄₋₁₅ | 7 | 98 | 1 | 1 | 7.9 |
| 13 | C ₁₂ | 4 | 95 | 4 | 1 | 17.9 |
| 14 | C ₁₂ | 4 | 95 | 1 | 4 | 32.3 |
| 15 | C ₁₂ | 4 | 98 | 1 | 1 | 37.4 |
| 16 | C ₁₂ | 23 | 95 | 4 | 1 | 24.5 |
| 17 | C ₁₂ | 23 | 95 | 1 | 4 | 34.2 |
| 18 | C ₁₂ | 23 | 98 | 1 | 1 | 1.5 |
| 19 | C ₁₆ | 20 | 95 | 4 | 1 | 25.7 |
| 20 | C ₁₆ | 20 | 95 | 1 | 4 | 11.8 |
| 21 | C ₁₆ | 20 | 98 | 1 | 1 | 17.4 |
| 22 | C ₁₈ | 2 | 95 | 4 | 1 | 8.5 |
| 23 | C ₁₈ | 2 | 95 | 1 | 4 | 7.9 |
| 24 | C ₁₈ | 2 | 98 | 1 | 1 | 5.5 |
| 25 | C ₁₈ | 10 | 95 | 4 | 1 | 16.8 |
| 26 | C ₁₈ | 10 | 95 | 1 | 4 | 6.2 |
| 27 | C ₁₈ | 10 | 98 | 1 | 1 | 3.7 |
| 28 | C ₁₈ | 20 | 95 | 4 | 1 | 13.6 |
| 29 | C ₁₈ | 20 | 95 | 1 | 4 | 28.4 |
| 30 | C ₁₈ | 20 | 98 | 1 | 1 | 5.3 |
| 31 | C ₄ | 1 | 95 | 4 | 1 | 6.2 |
| 32 | C ₄ | 1 | 95 | 1 | 4 | 11.7 |
| 33 | C ₄ | 1 | 98 | 1 | 1 | 1.0 |
| 34 | C ₄ | 2 | 95 | 4 | 1 | 33.9 |
| 35 | C ₄ | 2 | 95 | 1 | 4 | 34.1 |
| 36 | C ₄ | 2 | 98 | 1 | 1 | 38.7 |
| 37 | C ₁₁₋₁₄ | 12 | 95 | 4 | 1 | 24.1 |
| 38 | C ₁₁₋₁₄ | 12 | 95 | 1 | 4 | 33.1 |
| 39 | C ₁₁₋₁₄ | 12 | 98 | 1 | 1 | 10.2 |
| Control 4 | - | - | 99 | 0 | 1 | 2.2 |
| Control 5 | - | - | 96 | 0 | 4 | 9.5 |

Table 4A - Nonionic Surfactants (Commercially Available)

| Exp. | Surfactant Trade Name | n | pbw solvent | pbw surfactant | pbw water | ΔE |
|-----------|--------------------------|----|----------------|-------------------|--------------|------------|
| 40 | Triton X-405 | 40 | 95 | 4 | 1 | 37.7 |
| 41 | Triton X-405 | 40 | 95 | 1 | 4 | 25.5 |
| 42 | Triton X-405 | 40 | 98 | 1 | 1 | 15.9 |
| 43 | Igepal CA-520 | 5 | 95 | 4 | 1 | 4.4 |
| 44 | Igepal CA-520 | 5 | 95 | 1 | 4 | 10.0 |
| 45 | Igepal CA-520 | 5 | 98 | 1 | 1 | 2.3 |
| 46 | Igepal CO-850 | 20 | 95 | 4 | 1 | 4.0 |
| 47 | Igepal CO-850 | 20 | 95 | 1 | 4 | 2.6 |
| 48 | Igepal CO-850 | 20 | 98 | 1 | 1 | 16.2 |
| 49 | Span-80 | - | 95 | 4 | 1 | 3.7 |
| 50 | Span-80 | - | 95 | 1 | 4 | 2.4 |
| 51 | Span-80 | - | 98 | 1 | 1 | 5.2 |
| Control 1 | - | - | 99 | 0 | 1 | 2.2 |
| Control 2 | - | - | 96 | 0 | 4 | 9.5 |

Tables 4 and 4A show that nonionic surfactants in the presence of water enhance the cleaning and dye removal of the base cyclic siloxane (D₅) solvent.

Example 5 - Ionic Surfactants

A cleaning composition according to the present invention containing a cyclic siloxane (D₅), water and an ionic surfactant was made. Fabric swatches were cleaned using the above procedure, and the color difference was measured to determine the effectiveness of the cleaning composition. A solution of cyclic siloxane (D₅) and water without a surfactant was used as a control.

Table 5 - Ionic Surfactants

| Exp | Surfactant Trade Name | pbw solvent | pbw surfactant | pbw Water | ΔE |
|-----------|-----------------------|-------------|----------------|-----------|------------|
| 52 | Aerosol OT | 95 | 4 | 1 | 6.9 |
| 53 | Aerosol OT | 95 | 1 | 4 | 20.3 |
| 54 | Aerosol OT | 98 | 1 | 1 | 7.5 |
| 55 | Triton X-200 | 95 | 4 | 1 | 4.0 |
| 56 | Triton X-200 | 95 | 1 | 4 | 36.0 |
| 57 | Triton X-200 | 98 | 1 | 1 | 3.3 |
| 58 | Vari-Soft 300 | 95 | 4 | 1 | 40.3 |
| 59 | Vari-Soft 300 | 95 | 1 | 4 | 38.4 |
| 60 | Vari-Soft 300 | 98 | 1 | 1 | 35.9 |
| 61 | Bio-Soft D-62 | 95 | 4 | 1 | 2.9 |
| 62 | Bio-Soft D-62 | 95 | 1 | 4 | 28.4 |
| 63 | Bio-Soft D-62 | 98 | 1 | 1 | 14.3 |
| 64 | Ethoquad C/25 | 95 | 4 | 1 | 35.2 |
| 65 | Ethoquad C/25 | 95 | 1 | 4 | 34.3 |
| 66 | Ethoquad C/25 | 98 | 1 | 1 | 26.3 |
| 67 | Span-80 | 95 | 4 | 1 | 3.7 |
| 68 | Span-80 | 95 | 1 | 4 | 2.4 |
| 69 | Span-80 | 98 | 1 | 1 | 5.2 |
| 70 | Glucopon 225* | 95 | 1 | 4 | 4.7 |
| 71 | Glucopon 225 | 95 | 4 | 1 | 31.2 |
| 72 | Glucopon 225 | 98 | 1 | 1 | 5.8 |
| 73 | Glucopon 225 | 99 | 1 | - | 10.8 |
| 74 | Glucopon 425** | 95 | 1 | 4 | 32.5 |
| 75 | Glucopon 425 | 95 | 4 | 1 | 36.2 |
| 76 | Glucopon 425 | 98 | 1 | 1 | 19.0 |
| 77 | Glucopon 425 | 99 | 1 | - | 3.9 |
| 78 | Glucopon 600** | 95 | 1 | 4 | 4.3 |
| 79 | Glucopon 600 | 95 | 4 | 1 | 27.9 |
| 80 | Glucopon 600 | 98 | 1 | 1 | 4.7 |
| 81 | Glucopon 600 | 99 | 1 | - | 9.3 |
| 82 | Alkamide S-280 | 95 | 5 | - | 8.4 |
| 83 | Alkamide S-280 | 99 | 1 | - | 1.7 |
| 84 | Alkamide S-280 | 98 | 1 | 1 | 2.0 |
| 85 | Alkamide CME | 95 | 5 | - | 7.6 |
| 86 | Alkamide CME | 99 | 1 | - | 2.4 |
| 87 | Alkamide CME | 98 | 1 | 1 | 6.6 |
| Control 6 | - | 99 | 0 | 1 | 2.2 |
| Control 7 | - | 96 | 0 | 4 | 9.5 |

*30% water; **50% water

Table 5 shows that the ionic surfactants in the presence of water enhanced the water soluble dye removal of the base cyclic siloxane (D₅) solvent.

Table 6 - Ionic surfactants with and without water

| Exp | pbw solvent | Surfactant | pbw surfactant | pbw Water | ΔE |
|-----|-------------|---|----------------|-----------|------------|
| 88 | 14.25 | Cocoa/oleamidopropyl betaine (30% in water) | 0.75 | - | 14.39 |
| 89 | 14.85 | Cocoa/oleamidopropyl betaine (30% in water) | 0.15 | - | 16.76 |
| 90 | 14.7 | Cocoa/oleamidopropyl betaine (30% in water) | 0.15 | 0.15 | 32.02 |
| 91 | 14.25 | Cocomidopropyl betaine (29% in water) | 0.6 | - | 31.20 |
| 92 | 14.85 | Cocomidopropyl betaine (29% in water) | 0.15 | - | 7.11 |
| 93 | 14.7 | Cocomidopropyl betaine (29% in water) | 0.15 | 0.15 | 29.80 |
| 94 | 14.25 | Stearic acid monoethanolamide | 0.6 | - | 8.37 |
| 95 | 14.85 | Stearic acid monoethanolamide | 0.15 | - | 1.72 |
| 96 | 14.7 | Stearic acid monoethanolamide | 0.15 | 0.15 | 1.96 |
| 97 | 14.25 | Amphoteric surfactant (50% in water) | 0.6 | - | 33.76 |
| 98 | 14.85 | Amphoteric surfactant (50% in water) | 0.15 | - | 24.95 |
| 99 | 14.7 | Amphoteric surfactant (50% in water) | 0.15 | 0.15 | 32.09 |
| 100 | 14.25 | Coconut fatty acid monoethanolamide | 0.6 | - | 7.61 |
| 101 | 14.85 | Coconut fatty acid monoethanolamide | 0.15 | - | 2.40 |
| 102 | 14.7 | Coconut fatty acid monoethanolamide | 0.15 | 0.15 | 6.59 |
| 103 | 14.25 | 1,2-hexanediol | 0.6 | - | 3.86 |
| 104 | 14.85 | 1,2-hexanediol | 0.15 | - | 21.40 |
| 105 | 14.7 | 1,2-hexanediol | 0.15 | 0.15 | 14.85 |
| 106 | 14.85 | Di(ethyleneglycol)-2-ethylhexyl ether | 0.15 | - | 8.03 |
| 107 | 14.25 | Di(ethyleneglycol)-2-ethylhexyl ether | 0.75 | - | 10.40 |
| 108 | 14.25 | Di(ethyleneglycol)-2-ethylhexyl ether | 0.6 | 0.15 | 9.85 |
| 109 | 14.25 | Di(ethyleneglycol)-2-ethylhexyl ether | 0.15 | 0.6 | 13.97 |
| 110 | 14.7 | Di(ethyleneglycol)-2-ethylhexyl ether | 0.15 | 0.15 | 22.73 |
| 111 | 14.85 | Di(ethyleneglycol)hexyl ether | 0.15 | - | 8.89 |
| 112 | 14.25 | Di(ethyleneglycol)hexyl ether | 0.75 | - | 9.13 |
| 113 | 14.25 | Di(ethyleneglycol)hexyl ether | 0.6 | 0.15 | 33.40 |
| 114 | 14.25 | Di(ethyleneglycol)hexyl ether | 0.15 | 0.6 | 16.64 |
| 115 | 14.7 | Di(ethyleneglycol)hexyl ether | 0.15 | 0.15 | 24.02 |
| 116 | 14.85 | Didecyldimethylammonium bromide | 0.15 | - | 16.55 |
| 117 | 14.25 | Didecyldimethylammonium bromide | 0.75 | - | 15.44 |
| 118 | 14.25 | Didecyldimethylammonium bromide | 0.6 | 0.15 | 4.78 |
| 119 | 14.25 | Didecyldimethylammonium bromide | 0.15 | 0.6 | 10.36 |
| 120 | 14.7 | Didecyldimethylammonium bromide | 0.15 | 0.15 | 10.88 |
| 121 | 14.85 | Dihexadecyldimethylammonium bromide | 0.15 | - | 12.53 |
| 122 | 14.25 | Dihexadecyldimethylammonium bromide | 0.75 | - | 12.15 |
| 123 | 14.25 | Dihexadecyldimethylammonium bromide | 0.6 | 0.15 | 8.73 |
| 124 | 14.25 | Dihexadecyldimethylammonium bromide | 0.15 | 0.6 | 9.56 |
| 125 | 14.7 | Dihexadecyldimethylammonium bromide | 0.15 | 0.15 | 9.45 |
| 126 | 14.85 | Cetyltrimethylammonium bromide | 0.15 | - | 13.03 |
| 127 | 14.25 | Cetyltrimethylammonium bromide | 0.75 | - | 14.79 |
| 128 | 14.25 | Cetyltrimethylammonium bromide | 0.6 | 0.15 | 12.25 |
| 129 | 14.25 | Cetyltrimethylammonium bromide | 0.15 | 0.6 | 38.27 |
| 130 | 14.7 | Cetyltrimethylammonium bromide | 0.15 | 0.15 | 10.39 |
| 131 | 14.85 | 1,2-butanediol | 0.15 | - | 26.14 |
| 132 | 14.25 | 1,2-butanediol | 0.75 | - | 33.45 |
| 133 | 14.7 | 1,2-butanediol | 0.15 | 0.15 | 21.40 |
| 134 | 14.85 | 1,2-decanediol | 0.15 | - | 11.26 |

| | | | | | |
|-----|-------|-----------------|------|------|-------|
| 135 | 14.25 | 1,2-decanediol | 0.75 | - | 29.54 |
| 136 | 14.7 | 1,2-decanediol | 0.15 | 0.15 | 11.55 |
| 137 | 14.85 | 1,2-hexanediol | 0.15 | - | 10.01 |
| 138 | 14.25 | 1,2-hexanediol | 0.75 | - | 28.56 |
| 139 | 14.7 | 1,2-hexanediol | 0.15 | 0.15 | 32.51 |
| 140 | 14.85 | 1,6-hexanediol | 0.15 | - | 7.47 |
| 141 | 14.25 | 1,6-hexanediol | 0.75 | - | 5.16 |
| 142 | 14.7 | 1,6-hexanediol | 0.15 | 0.15 | 31.78 |
| 143 | 14.85 | 1,10-decanediol | 0.15 | - | 5.82 |
| 144 | 14.25 | 1,10-decanediol | 0.75 | - | 1.22 |
| 145 | 14.7 | 1,10-decanediol | 0.15 | 0.15 | 8.33 |

Table 7 shows the variations in R and x that were explored for these surfactants. Mixtures of materials within a class were also examined as seen in experiments 13-16 and 29-34. None of these surfactants were soluble in D5 in the ranges examined but some were only slightly hazy. As seen in Table 1, the surfactants with $R=C_{12-15}$ and $x=3-9$ repeat units gave the best cleaning.

Table 7 - Ethoxylated Alcohols.

| Exp. | Surfactant | R | n | pbw | ΔE |
|-----------|------------------------------|-----------------|-------|-----------|------------|
| 146 | 06383 | C_4 | 1 | 1 | 1.9 |
| 147 | | C_4 | 1 | 5 | 2.7 |
| 148 | 2-(2-n-butoxy ethoxy)ethanol | C_4 | 2 | 1 | 3.2 |
| 149 | 067012 | C_4 | 2 | 5 | 3.2 |
| 150 | Neodol 25-3 | C_{12-15} | 3 | 1 | 38.8 |
| 151 | | C_{12-15} | 3 | 5 | 41.9 |
| 152 | Neodol 23-9 | C_{12-13} | 9 | 1 | 37.8 |
| 153 | | C_{12-13} | 9 | 5 | 38.7 |
| 154 | Neodol 23-6.5 | C_{12-13} | 6.5 | 1 | 39.1 |
| 155 | | C_{12-13} | 6.5 | 5 | 38.6 |
| 156 | Neodol 45-7 | C_{14-15} | 7 | 1 | 18.7 |
| 157 | | C_{14-15} | 7 | 5 | 36.7 |
| 158 | | C_{14-15} | 7 | 5 | 30.7 |
| 159 | | C_{12-13}/C_4 | 6.5/1 | 5 (50/50) | 41.5 |
| 160 | | C_{12-13}/C_4 | 9/1 | 5 (50/50) | 42.9 |
| 161 | | C_{12-13}/C_4 | 3/1 | 5 (50/50) | 13.8 |
| 162 | | C_{14-15}/C_4 | 7/1 | 5 (50/50) | 41.1 |
| 163 | BRIJ 30 | C_{12} | 4 | 1 | 35.8 |
| 164 | 067220 | C_{12} | 4 | 5 | 40.7 |
| 165 | BRIJ 35 | C_{12} | 23 | 1 | 0.9 |
| 166 | 067219 | C_{12} | 23 | 5 | 1.3 |
| 167 | BRIJ 58 | C_{16} | 20 | 1 | 4.6 |
| 168 | | C_{16} | 20 | 5 | 2.0 |
| 169 | BRIJ 72 | C_{18} | 2 | 1 | 2.6 |
| 170 | 067263 | C_{18} | 2 | 5 | 19.0 |
| 171 | BRIJ 76 | C_{18} | 10 | 1 | 2.4 |
| 172 | 067262 | C_{18} | 10 | 5 | 23.4 |
| 173 | BRIJ 78 | C_{18} | 20 | 1 | 4.0 |
| 174 | | C_{18} | 20 | 5 | 22.8 |
| 175 | | C_{12}/C_4 | 4/1 | 5 (50/50) | 41.1 |
| 176 | | C_{12}/C_4 | 23/1 | 5 (50/50) | 1.6 |
| 177 | | C_{16}/C_4 | 2/1 | 5 (50/50) | 3.7 |
| 178 | | C_{16}/C_4 | 2/1 | 5 (50/50) | 11.4 |
| 179 | | C_{18}/C_4 | 10/1 | 5 (50/50) | 21.1 |
| 180 | | C_{18}/C_4 | 20/1 | 5 (50/50) | 34.4 |
| Control I | | -- | -- | 0 | 1.9 |

When similar compositions of 1 and D₅ with water were examined, again, the best cleaning was seen with R=C₁₂₋₁₅ and x=3-9 repeat units (Table 2).

Table 2. Ethoxylated Alcohols with Water.

| Exp. No. | Surfactant | R | n | pbw solvent | pbw surfactant | pbw water | ΔE |
|-----------|---------------|--------------------|-----|-------------|----------------|-----------|------|
| 35 | Neodol 23-6.5 | C ₁₂₋₁₃ | 6.5 | 95 | 4 | 1 | 39.5 |
| 36 | | C ₁₂₋₁₃ | 6.5 | 95 | 1 | 4 | 33.1 |
| 37 | | C ₁₂₋₁₃ | 6.5 | 98 | 1 | 1 | 13.8 |
| 38 | Neodol 23-9 | C ₁₂₋₁₃ | 9 | 95 | 4 | 1 | 34.9 |
| 39 | | C ₁₂₋₁₃ | 9 | 95 | 1 | 4 | 38.3 |
| 40 | | C ₁₂₋₁₃ | 9 | 98 | 1 | 1 | 25.5 |
| 41 | Neodol 25-3 | C ₁₂₋₁₅ | 3 | 95 | 4 | 1 | 7.7 |
| 42 | | C ₁₂₋₁₅ | 3 | 95 | 1 | 4 | 38.3 |
| 43 | | C ₁₂₋₁₅ | 3 | 98 | 1 | 1 | 38.9 |
| 44 | Neodol 45-7 | C ₁₄₋₁₅ | 7 | 95 | 4 | 1 | 34.5 |
| 45 | | C ₁₄₋₁₅ | 7 | 95 | 1 | 4 | 36.4 |
| 46 | | C ₁₄₋₁₅ | 7 | 98 | 1 | 1 | 7.9 |
| 47 | BRIJ 30 | C ₁₂ | 4 | 95 | 4 | 1 | 17.9 |
| 48 | | C ₁₂ | 4 | 95 | 1 | 4 | 32.3 |
| 49 | | C ₁₂ | 4 | 98 | 1 | 1 | 37.4 |
| 50 | BRIJ 35 | C ₁₂ | 23 | 95 | 4 | 1 | 24.5 |
| 51 | | C ₁₂ | 23 | 95 | 1 | 4 | 34.2 |
| 52 | | C ₁₂ | 23 | 98 | 1 | 1 | 1.5 |
| 53 | BRIJ 58 | C ₁₆ | 20 | 95 | 4 | 1 | 25.7 |
| 54 | | C ₁₆ | 20 | 95 | 1 | 4 | 11.8 |
| 55 | | C ₁₆ | 20 | 98 | 1 | 1 | 17.4 |
| 56 | BRIJ 72 | C ₁₈ | 2 | 95 | 4 | 1 | 8.5 |
| 57 | | C ₁₈ | 2 | 95 | 1 | 4 | 7.9 |
| 58 | | C ₁₈ | 2 | 98 | 1 | 1 | 5.5 |
| 59 | BRIJ 76 | C ₁₈ | 10 | 95 | 4 | 1 | 16.8 |
| 60 | | C ₁₈ | 10 | 95 | 1 | 4 | 6.2 |
| 61 | | C ₁₈ | 10 | 98 | 1 | 1 | 3.7 |
| 62 | BRIJ 78 | C ₁₈ | 20 | 95 | 4 | 1 | 13.6 |
| 63 | | C ₁₈ | 20 | 95 | 1 | 4 | 28.4 |
| 64 | | C ₁₈ | 20 | 98 | 1 | 1 | 5.3 |
| 65 | 06383 | C ₄ | 1 | 95 | 4 | 1 | 6.2 |
| 66 | | C ₄ | 1 | 95 | 1 | 4 | 11.7 |
| 67 | | C ₄ | 1 | 98 | 1 | 1 | 1.0 |
| 68 | 067012 | C ₄ | 2 | 95 | 4 | 1 | 33.9 |
| 69 | | C ₄ | 2 | 95 | 1 | 4 | 34.1 |
| 70 | | C ₄ | 2 | 98 | 1 | 1 | 38.7 |
| 71 | | C ₁₁₋₁₄ | 12 | 95 | 4 | 1 | 24.1 |
| 72 | | C ₁₁₋₁₄ | 12 | 95 | 1 | 4 | 33.1 |
| 73 | | C ₁₁₋₁₄ | 12 | 98 | 1 | 1 | 10.2 |
| Control 2 | | - | - | 95 | 0 | 1 | 5.3 |
| Control 3 | | - | - | 99 | 0 | 4 | 2.9 |
| Control 4 | | - | - | 99 | 0 | 5 | 2.6 |

Ethoxylated phenols, 2, were also explored (Table 3). The most effective mixtures included longer EO chains and lower amounts of water.

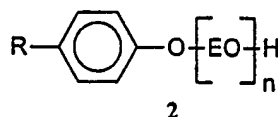


Table 3. Alkyl Phenol Surfactants.

| Exp. | Surfactant | R | n | pbw solvent | pbw surfactant | pbw water | ΔE |
|------|---------------|-----------------|----|-------------|----------------|-----------|------------|
| 74 | Triton X-405 | C ₉ | 40 | 95 | 4 | 1 | 37.7 |
| 75 | | | 40 | 95 | 1 | 4 | 25.5 |
| 76 | | | 40 | 98 | 1 | 1 | 15.9 |
| 77 | Igepal CA-520 | C ₁₂ | 5 | 95 | 4 | 1 | 4.4 |
| 78 | | | 5 | 95 | 1 | 4 | 10.0 |
| 79 | | | 5 | 98 | 1 | 1 | 2.3 |
| 80 | Igepal CO-850 | C ₉ | 20 | 95 | 4 | 1 | 4.0 |
| 81 | | | 20 | 95 | 1 | 4 | 2.6 |
| 82 | | | 20 | 98 | 1 | 1 | 16.2 |

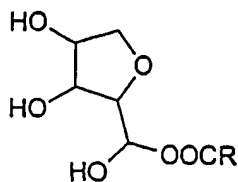
Glycol ethers and diols were also examined as additives to enhance the cleaning ability of the silicone solvent as seen in Table 4.

Table 4. Non-Ionic Ether and Diol Surfactants.

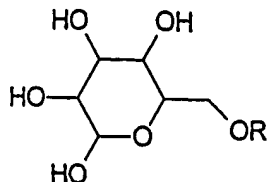
| Exp. No. | Surfactant | | pbw solvent | pbw surfactant | pbw water | ΔE |
|----------|------------|---------------------------------------|-------------|----------------|-----------|------------|
| 83 | AZ7989 | di(ethyleneglycol)-2-ethylhexyl ether | 99 | 1 | - | 8.03 |
| 84 | | | 95 | 5 | - | 10.40 |
| 85 | | | 95 | 4 | 1 | 9.85 |
| 86 | | | 95 | 1 | 4 | 13.97 |
| 87 | | | 98 | 1 | 1 | 22.73 |
| 88 | AZ7988 | di(ethyleneglycol)hexyl ether | 99 | 1 | - | 8.89 |
| 89 | | | 95 | 5 | - | 9.13 |
| 90 | | | 95 | 4 | 1 | 33.40 |
| 91 | | | 95 | 1 | 4 | 16.64 |
| 92 | | | 98 | 1 | 1 | 24.02 |
| 93 | AZ7997 | 1,2-butanediol | 99 | 1 | - | 26.14 |
| 94 | | | 95 | 5 | - | 33.45 |
| 95 | | | 98 | 1 | 1 | 21.40 |
| 96 | AZ7998 | 1,2-decanediol | 99 | 1 | - | 11.26 |
| 97 | | | 95 | 5 | - | 29.54 |
| 98 | | | 98 | 1 | 1 | 11.55 |
| 99 | AZ7995 | 1,2-hexanediol | 99 | 1 | - | 10.01 |
| 100 | | | 95 | 5 | - | 28.56 |
| 101 | | | 95 | 5 | - | 15.7 |
| 102 | | | 98 | 1 | 1 | 32.51 |
| 103 | | | 99 | 1 | - | 21.40 |
| 104 | | | 98 | 1 | 1 | 14.85 |
| 105 | AZ7996 | 1,6-hexanediol | 99 | 1 | - | 7.47 |
| 106 | | | 95 | 5 | - | 5.16 |
| 107 | | | 98 | 1 | 1 | 31.78 |
| 108 | AZ7999 | 1,10-decanediol | 99 | 1 | - | 5.82 |
| 109 | | | 95 | 5 | - | 1.22 |
| 110 | | | 98 | 1 | 1 | 8.33 |

- 5 In the ether examples, optimal performance was seen with the addition of small amounts of water. The 1,2-diols were efficient at removing the dye at the 5% level, although significant cleaning was seen at 1% with water present.

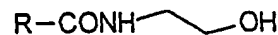
Table 5 shows the results from using sugar based surfactants and alkanol amides as water-based stain removers.



3
Span



4
Glucocon



5
Alkamide

Table 5. Other Non-Ionic Surfactants.

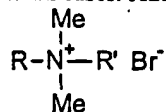
| Exp. No. | Surfactant Trade Name | R | pbw solvent | pbw surfactant | pbw water | ΔE |
|----------|-----------------------|--------------------|-------------|----------------|-----------|------------|
| 111 | Span-80 | Oleic | 95 | 4 | 1 | 3.7 |
| 112 | | | 95 | 1 | 4 | 2.4 |
| 113 | | | 98 | 1 | 1 | 5.2 |
| 114 | Glucocon 225* | C ₈₋₁₀ | 95 | 1 | 4 | 4.7 |
| 115 | | | 95 | 4 | 1 | 31.2 |
| 116 | | | 98 | 1 | 1 | 5.8 |
| 117 | | | 99 | 1 | - | 10.8 |
| 118 | Glucocon 425** | C ₈₋₁₆ | 95 | 1 | 4 | 32.5 |
| 119 | | | 95 | 4 | 1 | 36.2 |
| 120 | | | 98 | 1 | 1 | 19.0 |
| 121 | | | 99 | 1 | - | 3.9 |
| 122 | | | 95 | 5 | - | 19.6 |
| 123 | Glucocon 600*** | C ₁₀₋₁₆ | 95 | 1 | 4 | 4.3 |
| 124 | | | 95 | 4 | 1 | 27.9 |
| 125 | | | 98 | 1 | 1 | 4.7 |
| 126 | | | 99 | 1 | - | 9.3 |
| 127 | Alkamide S-280 | Stearic | 95 | 5 | - | 8.37 |
| 128 | | | 99 | 1 | - | 1.72 |
| 129 | | | 98 | 1 | 1 | 1.96 |
| 130 | Alkamide CME | Coconut | 95 | 5 | - | 7.61 |
| 131 | | | 99 | 1 | - | 2.40 |
| 132 | | | 98 | 1 | 1 | 6.59 |

*30% water, ** 50% water, *** 50% water

The sorbitan oleate, as Span 80, was fairly ineffective as a cleaning additive, but the 6-membered glucoside materials (Glucocons) exhibited good cleaning power at the 4% level with additional water. The two alkanol amides performed poorly as cleaning surfactants in these tests.

Cationics

The cationic surfactants tested were all quaternary ammonium salts of the type 6 below. As one can see, the quat salts were effective at the 1% level in all cases. Additional water was sometimes advantageous.



6

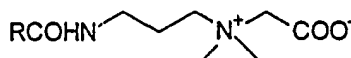
Table 6. Cationic Surfactants.

| Exp. No. | Surfactant | | pbw solvent | pbw surfactant | pbw water | ΔE |
|----------|------------|--|-------------|----------------|-----------|------------|
| 133 | AZ7987 | Didecyltrimethyl ammonium bromide | 99 | 1 | - | 16.55 |
| 134 | | | 95 | 5 | - | 15.44 |
| 135 | | | 95 | 4 | 1 | 4.78 |
| 136 | | | 95 | 1 | 4 | 10.36 |
| 137 | | | 98 | 1 | 1 | 10.88 |
| 138 | AZ7990 | Di-hexadecyltrimethyl ammonium bromide | 99 | 1 | - | 12.53 |
| 139 | | | 95 | 5 | - | 12.15 |
| 140 | | | 95 | 4 | 1 | 8.73 |
| 141 | | | 95 | 1 | 4 | 9.56 |
| 142 | | | 98 | 1 | 1 | 9.45 |
| 143 | AZ7991 | cetyltrimethylammonium bromide | 99 | 1 | - | 13.03 |
| 144 | | | 95 | 5 | - | 14.79 |
| 145 | | | 95 | 4 | 1 | 12.25 |
| 146 | | | 95 | 1 | 4 | 38.27 |
| 147 | | | 98 | 1 | 1 | 10.39 |
| 148 | | Vari-Soft 300 | 95 | 4 | 1 | 40.3 |
| 149 | | | 95 | 1 | 4 | 38.4 |
| 150 | | | 98 | 1 | 1 | 35.9 |
| 151 | 06955 | Ethoquad C/25 | 95 | 4 | 1 | 35.2 |
| 152 | | | 95 | 1 | 4 | 34.3 |
| 153 | | | 98 | 1 | 1 | 26.3 |
| 154 | | | 99 | 1 | - | 41.5 |
| 155 | | | 95 | 5 | - | 41.2 |

Vari-Soft 300: 30% $(C_{16})Me_3N^+Cl^-$; Ethoquad C/25: $C_{12-15}(Me)N((EO)_{25}H)_2^+Cl^-$

Amphoterics

- 5 The amphoteric materials examined were of the betaine class as illustrated below (table 7). These were quaternized glycine derivatives. All these materials were supplied as aqueous solutions and performed moderately well at high levels and even better at lower, 1% loading.



10

7

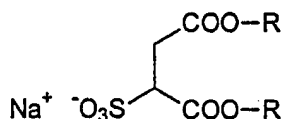
Table 7. Amphoteric Surfactants.

| Exp. No. | Surfactant | R | pbw solvent | pbw surfactant | pbw water | ?E |
|----------|---------------------|-----------|-------------|----------------|-----------|-------|
| 156 | Mirataine COB* | Coco/oleo | 95 | 5 | - | 14.39 |
| 157 | | | 99 | 1 | - | 16.76 |
| 158 | | | 98 | 1 | 1 | 32.02 |
| 159 | Mirataine BET-C30** | Coco | 95 | 5 | - | 31.20 |
| 160 | | | 99 | 1 | - | 7.11 |
| 161 | | | 98 | 1 | 1 | 29.80 |
| 162 | Mirataine JC HA*** | | 95 | 5 | - | 33.76 |
| 163 | | | 99 | 1 | - | 24.95 |
| 164 | | | 98 | 1 | 1 | 32.09 |

*coca/oleamidopropyl betaine 30% in water, ** cocamidopropyl betaine 29% in water, *** amphoteric 50% in water

Anionics

- 5 A wide variety of organic anionic surfactants are available in the forms of sulfosuccinates, sulfonates, phosphonates and the like. One set examined were the sulfosuccinates as shown in Table 8. Best results were seen with high levels of added water. One beneficial feature of the Aerosol OT was that it was soluble in D₅ to at least 5 weight percent.



10

Table 8. Sulfosuccinates.

| Exp. | Surfactant Trade Name | R | mixture | pbw solvent | pbw surf | pbw water | ΔE |
|------|-----------------------|----------|---------|-------------|----------|-----------|------|
| 165 | Aerosol TR | Tridecyl | - | 99 | 1 | - | 2.8 |
| 166 | | | - | 95 | 5 | - | 6.5 |
| 167 | Aerosol OT | Octyl | - | 99 | 1 | - | 1.6 |
| 168 | | | - | 95 | 5 | - | 2.3 |
| 169 | | | - | 95 | 4 | 1 | 6.9 |
| 170 | | | - | 95 | 1 | 4 | 20.3 |
| 171 | | | - | 98 | 1 | 1 | 7.5 |
| 172 | Aerosol GPG | Octyl | - | 99 | 1 | - | 3.0 |
| 173 | | | - | 95 | 5 | - | 3.0 |
| 174 | Aerosol TR/OT | | 50/50 | 99 | 1 | - | 1.5 |
| 175 | | | 50/50 | 95 | 5 | - | 2.5 |
| 176 | Aerosol TR/GPG | | 50/50 | 99 | 1 | - | 6.9 |
| 177 | | | 50/50 | 95 | 5 | - | 16.9 |
| 178 | Aerosol OT/GPG | | 50/50 | 99 | 1 | - | 4.6 |
| 179 | | | 50/50 | 95 | 5 | - | 6.7 |

Several phosphorous containing surfactants were tested as shown in Table 9. The ethoxylated phosphonates exhibited modest cleaning behavior while the lecithin-based surfactants did not remove the water soluble dye from the swatch.

15

Table 9. Phosphorous Containing Anionic Surfactants.

| Exp. No. | Surfactant Trade Name | Pbw Solvent | pbw surfactant | pbw water | ΔE |
|----------|-----------------------|-------------|----------------|-----------|------------|
| 180 | ATPHOS 3250 | 99 | 1 | - | 11.5 |
| 181 | | 95 | 5 | - | 12.3 |
| 182 | | 95 | 4 | 1 | 7.9 |
| 183 | | 95 | 1 | 4 | 10.1 |
| 184 | ATPHOS 3226 | 98 | 1 | 1 | 13.5 |
| 185 | | 99 | 1 | - | 12.2 |
| 186 | | 95 | 5 | - | 11.4 |
| 187 | | 95 | 4 | 1 | 11.9 |
| 188 | YELKIN TS | 95 | 1 | 4 | 6.8 |
| 189 | | 98 | 1 | 1 | 4.7 |
| 190 | | 99 | 1 | - | 6.8 |
| 191 | | 95 | 5 | - | 20.7 |
| 192 | Ultralec F | 95 | 4 | 1 | 7.5 |
| 193 | | 95 | 1 | 4 | 8.2 |
| 194 | | 98 | 1 | 1 | 4.9 |
| 195 | | 99 | 1 | - | 1.9 |
| 196 | | 95 | 5 | - | 1.4 |
| 197 | | 95 | 4 | 1 | 1.7 |
| 198 | | 95 | 1 | 4 | 1.8 |
| 199 | | 98 | 1 | 1 | 3.3 |

ATPHOS 3250: $C_{12}\text{-Ph-O-(EO)}_4\text{-P}_2\text{O}_5^-$; ATPHOS 3226: $C_{13}\text{-Ph-O-(EO)}_6\text{-P}_2\text{O}_5^-$; Yelkin and Ultralec are lecithin based.

5

Alkyl and aryl sulfonates were also explored as surfactants for the silicone solvent. Table 10 shows the results of such materials, with and without additional water.

Table 10. Other Anionic Surfactants.

| Exp | Surfactant | Surfactant Trade Name | pbw solvent | pbw surfactant | pbw Water | ΔE |
|-----|------------|---------------------------------|-------------|----------------|-----------|------------|
| 200 | AZ6005 | Witconate AOS | 95 | 5 | - | 11.9 |
| 201 | | | 95 | 5 | - | 3.9 |
| 202 | | | 99 | 1 | - | 9.7 |
| 203 | | | 99 | 1 | - | 11.2 |
| 204 | | | 99 | 1 | - | 11.8 |
| 205 | | | 99 | 1 | - | 6.4 |
| 206 | | | 99 | 1 | - | 18.3 |
| 207 | | | 99 | 1 | - | 8.2 |
| 208 | 06417 | $C_{12}\text{-SO}_4\text{Na}^+$ | 99 | 1 | - | 2.7 |
| 209 | | | 95 | 5 | - | 3.4 |
| 210 | 06206 | Triton X-200 | 99 | 1 | - | 6.2 |
| 211 | | | 95 | 5 | - | 5.3 |
| 212 | | | 95 | 4 | 1 | 11.6 |
| 213 | | | 95 | 1 | 4 | 4.8 |
| 214 | | | 98 | 1 | 1 | 19.0 |
| 215 | 06651 | DDBSA | 99 | 1 | - | 51.5 |
| 216 | | | 95 | 5 | - | 50.4 |
| 217 | | | 95 | 4 | 1 | 52.3 |
| 218 | | | 95 | 1 | 4 | 47.4 |
| 219 | | | 98 | 1 | 1 | 49.1 |
| 220 | 067751 | Bio-Soft D-62 | 95 | 4 | 1 | 2.9 |
| 221 | | | 95 | 1 | 4 | 28.4 |
| 222 | | | 98 | 1 | 1 | 14.3 |

Triton X-200: $C_{12}\text{-Ph-O-(EO)}_3\text{-OSO}_3\text{Na}^+$; Witconate AOS: $C_{14-16}\text{-SO}_4\text{Na}^+$; Bio-Soft D-62: Na DDBSA, 50%.

Fluoro-surfactants were also examined as shown in Table 11. Of all the varieties tried, the fluorinated quat salts and the fluoroalkyl alkoxide displayed the best performance.

5

Table 11. Fluoro-Surfactants.

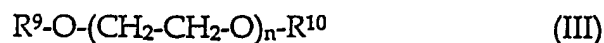
| Exp. No. | Surfactant Trade Name | Type | pbw solvent | pbw surfactant | pbw water | ΔE |
|----------|-----------------------|--|-------------|----------------|-----------|------------|
| 223 | Fluorad FC-120 | $F_{2n+1}C_n\text{SO}_3^-\text{NR}_4^+$ | 99 | 1 | - | 8.5 |
| 224 | Fluorad FC-120 | | 98 | 1 | 1 | 8.1 |
| 225 | Fluorad FC-129 | $F_{2n+1}C_n\text{COO}^-\text{K}^+$ | 99 | 1 | - | 1.9 |
| 226 | Fluorad FC-129 | | 98 | 1 | 1 | 7.4 |
| 227 | Fluorad FC-135 | $(F_{2n+1}C_n)_4\text{N}^+\text{T}^-$ | 99 | 1 | - | 13.0 |
| 228 | Fluorad FC-135 | | 98 | 1 | 1 | 31.9 |
| 229 | Fluorad FC-170C | $F_{2n+1}C_n\text{-(EO)}_x\text{-H}$ | 99 | 1 | - | 10.6 |
| 230 | Fluorad FC-170C | | 98 | 1 | 1 | 13.0 |
| 231 | Fluorad FC-171 | $F_{2n+1}C_n\text{-OR}$ | 99 | 1 | - | 7.5 |
| 232 | Fluorad FC-171 | | 98 | 1 | 1 | 21.7 |
| 233 | Fluorad FC-430 | $F_{2n+1}C_n\text{-COOR}$ | 99 | 1 | - | 10.9 |
| 234 | Fluorad FC-430 | | 98 | 1 | 1 | 10.4 |
| 235 | Fluorad FC-740 | $F_{2n+1}C_n\text{-COOR}$ | 99 | 1 | - | 2.2 |
| 236 | Fluorad FC-740 | | 98 | 1 | 1 | 3.9 |
| 237 | Dynol 604 | $F_{2n+1}C_n\text{SO}_2\text{N(Et)CH}_2\text{COO}^-\text{K}^+$ | 99 | 1 | - | 7.1 |
| 238 | Dynol 604 | | 98 | 1 | 1 | 1.2 |

The present invention exhibits improved performance of dry cleaning agents for stain removal, particularly water soluble stains, through the addition of a surfactant, and optionally water.

CLAIMS:

1. A dry cleaning composition, comprising a volatile cyclic, linear or branched siloxane, or combination thereof, and one or more organic surfactants.
- 5 2. The composition of Claim 1, comprising from about 90 to about 99.99 parts by weight of the volatile siloxane and from about 0.001 to less than 10 parts by weight of the surfactant or combination of surfactants.
3. The composition of Claim 2, further comprising from about 0.01 to about 15 parts by weight of water.
- 10 4. The composition of Claim 1, wherein the surfactant or surfactants are selected from the classes of nonionic, cationic, anionic and amphoteric surfactants.
5. The composition of Claim 1, wherein the organic surfactant comprises a mixture of two or more compatible surfactants of the same or
15 different classes.
6. The composition of Claim 1, wherein the organic surfactant is a nonionic surfactant.

7. The composition of Claim 6, wherein the surfactant comprises one or more nonionic surfactants according to one or more of the structural formulas III and IV:

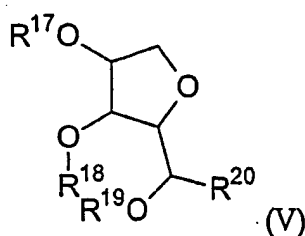


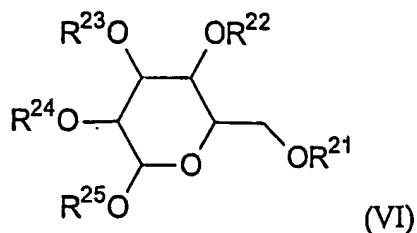
wherein:

R^9 is a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, branched, unsaturated, aromatic and fluoro containing hydrocarbon radicals, R^{10} is hydrogen or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, branched, unsaturated, aromatic and fluoro containing hydrocarbon radicals, and n is from about 1 to about 100.

8. The composition of Claim 8, wherein R^9 contains from 2 to about 24 carbons, R^{10} is H and n is from about 2 to about 20.

15 9. The composition of Claim 6, wherein the surfactant comprises one or more nonionic surfactants according to one or more of the structural formulas V and VI:





wherein:

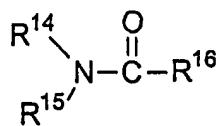
each R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , R^{24} and R^{25} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen containing hydrocarbon radicals.

10. The composition of Claim 9, wherein R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , R^{24} and R^{25} are each H or a hydrocarbon group of 1 to 24 carbons.

11. The composition of Claim 10, wherein one of R^{17} and R^{20} is a hydrocarbon of from 8 to 24 carbons while the other is H or a hydrocarbon of from 1 to 4 carbons, such as $-\text{CH}_2\text{OH}$ or $-\text{CH}_2\text{CH}_3$, and one of R^{21} and R^{25} is H or a hydrocarbon of from 8 to 24 carbons while the other is a hydrocarbon of from 1 to 4 carbons, such as $-\text{CH}_2\text{OH}$ or $-\text{CH}_2\text{CH}_3$.

12. The composition of Claim 11, wherein the nonionic surfactant or surfactants are chosen from sucrose esters, glucose esters, monoglycerides, polysaccharide ethers and sorbitan-based surfactants.

13. The composition of Claim 6, wherein the surfactant comprises one or more nonionic surfactants selected from the group consisting of an amine-based surfactant and a phosphate ester-based surfactant according to the structural formulas VII and VIII:



(VII)

(VIII)

wherein:

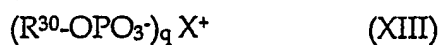
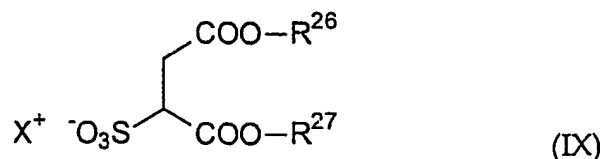
each R¹¹, R¹², R¹³, R¹⁴, R¹⁵, and R¹⁶ is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, branched, unsaturated, aromatic, and fluoro containing hydrocarbon radicals and chalcogen containing hydrocarbon radicals.

14. The composition of Claim 13, wherein two of R¹¹, R¹² and R¹³, are H or hydrocarbon groups of 1 to 4 carbons, and one is a hydrocarbon group of from 8 to 24 carbons, and R¹⁴ and R¹⁵ are either H or hydrocarbon groups of from 1 to 4 carbons while R¹⁶ is a hydrocarbon group of from 8 to 24 carbons, or R¹⁴ and R¹⁵ are hydrocarbon groups of from 8 to 24 carbons while R¹⁶ is a hydrocarbon group of from 1 to 4 carbons.

15. The composition of Claim 14, wherein the nonionic surfactant or surfactants are chosen from alkanol amides, amine oxides, ethoxylated amines, ethoxylated amides and phosphate esters.

16. The composition of Claim 1, wherein the organic surfactant is an anionic surfactant.

17. The composition of Claim 16, wherein the surfactant comprises one or more anionic surfactants selected from the group consisting of a sulfosuccinate, sulfate, sulfonate, carboxylate, or phosphorous containing surfactant according to the structural formulas IX to XIII:



wherein:

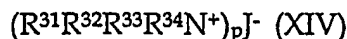
each R^{26} , R^{27} , R^{28} , R^{29} and R^{30} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen containing hydrocarbon radicals, and X is a cation selected from the group consisting of H, alkali metals, alkaline earth metals or chalcogen containing cations wherein q is the oxidation state or valence of X and whereby X does not unduly interfere with the functioning of the molecule as a surfactant.

18. The composition of Claim 17, wherein R^{26} and R^{27} are linear hydrocarbon groups of from 4 to 20 carbons, R^{28} is a hydrocarbon group of from 6 to 20 carbons, R^{29} is a hydrocarbon group of from 8 to 26 carbons, and R^{30} is a hydrocarbon of from 8 to 30 carbons.

5 19. The composition of Claim 18, wherein R^{26} and R^{27} are linear hydrocarbon groups of from 6 to 13 carbons, R^{28} is a hydrocarbon group of from 8 to 16 carbons, and R^{29} is a hydrocarbon group of from 10 to 20 carbons.

20. The composition of Claim 1, wherein the organic surfactant is a cationic surfactant.

10 21. The composition of Claim 20, wherein the surfactant comprises one or more cationic surfactants that may be a quaternary amine-based surfactant according to the structural formula XIV:



wherein:

15 each R^{31} , R^{32} , R^{33} , and R^{34} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen containing hydrocarbon radicals, and j is a suitable anion having a valence or oxidation state p that does not unduly interfere with the functioning of the molecule as a surfactant.

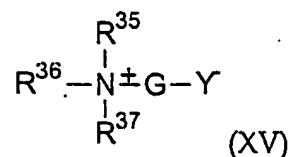
20

22. The composition of Claim 21, wherein R^{31} and R^{32} are hydrocarbon groups of from 1 to 4 carbons, and R^{33} and R^{34} are hydrocarbon groups of from 6 to 30 carbons.

23. The composition of Claim 22, wherein R^{31} and R^{32} are methyl,
25 and R^{33} and R^{34} are hydrocarbon groups of from 8 to 24 carbons.

24. The composition of Claim 1, wherein the organic surfactant is an amphoteric surfactant.

25. The composition of Claim 24, wherein the surfactant comprises one or more amphoteric surfactants according to the structural formula XV:



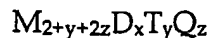
5

wherein:

each R^{35} , R^{36} and R^{37} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen
10 containing hydrocarbon radicals, G is a divalent spacer group, and Y is a carboxylate, sulfonate, sulfate, phosphonate or other similar group.

26. The composition of Claim 25, wherein R^{35} is a hydrocarbon of from 1 to 4 carbons, and R^{36} and R^{37} are hydrocarbons of from 6 to 24 carbons.

27. The composition of Claim 1, wherein the linear or branched, volatile siloxane comprises one or more compounds of the structural formula:



wherein:

5 M is $R^1_3SiO_{1/2}$;

D is $R^2R^3SiO_{2/2}$;

T is $R^4SiO_{3/2}$;

and Q is $SiO_{4/2}$

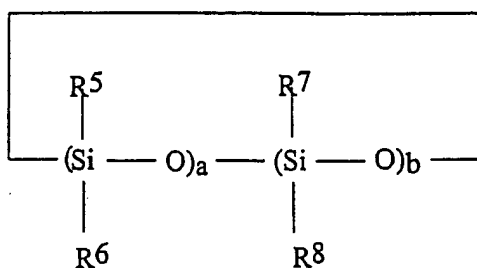
R^1 , R^2 , R^3 and R^4 are each independently a monovalent hydrocarbon radical;

10 and

x and y are each integers, wherein $0 \leq x \leq 10$ and $0 \leq y \leq 10$ and $0 \leq z \leq$

10.

28. The composition of Claim 1, wherein the cyclic siloxane component comprises one or more compounds of the structural formula:



15

wherein:

R^5 , R^6 , R^7 and R^8 are each independently a monovalent hydrocarbon group;

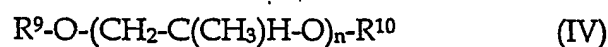
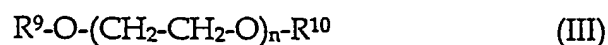
and

a and b are each integers wherein $0 \leq a \leq 10$ and $0 \leq b \leq 10$, provided that $3 \leq$

20 $(a + b) \leq 10$.

29. A method for dry cleaning an article, comprising contacting the article with a composition comprising a cyclic, linear or branched siloxane and one or more organic surfactants selected from the classes of nonionic, cationic, anionic and amphoteric surfactants.

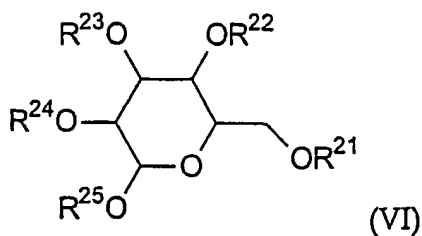
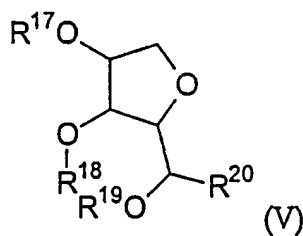
30. The method of Claim 29, wherein the surfactant comprises one or more nonionic surfactants according to one or more of the structural formulas III and IV:



wherein:

R^9 is a monovalent hydrocarbon group of 1 to 30 carbons that may be linear, cyclic, branched, unsaturated, aromatic or fluoro containing, R^{10} is hydrogen or a monovalent hydrocarbon group of 1 to 30 carbons that may be linear, cyclic, branched, unsaturated, aromatic or fluoro containing, and n is from about 1 to about 100.

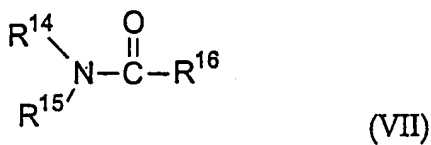
31. The method of Claim 29, wherein the surfactant comprises one or more nonionic surfactants according to one or more of the structural formulas V and VI:



wherein:

each R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴ and R²⁵ is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen containing hydrocarbon radicals.

32. The method of Claim 29, wherein the surfactant comprises one or more nonionic surfactants that may be an amine-based or phosphate ester-based surfactant according to one or more of the structural formulas VII and VIII:

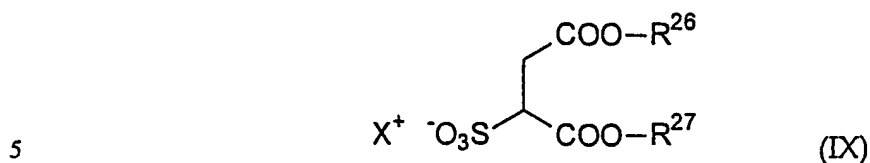


(VIII)

wherein:

each R¹¹, R¹², R¹³, R¹⁴, R¹⁵, and R¹⁶ is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen containing hydrocarbon radicals.

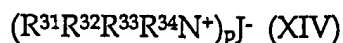
33. The method of Claim 29, wherein the surfactant comprises one or more anionic surfactants that may be a sulfosuccinate, sulfate, sulfonate, carboxylate, or phosphorous containing surfactant according to one or more of the structural formulas IX to XIII:



10 wherein:

each R^{26} , R^{27} , R^{28} , R^{29} and R^{30} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen containing hydrocarbon radicals, and X is a cation
15 selected from the group consisting of H, alkali metals, alkaline earth metals or chalcogen containing cations wherein q is the oxidation state or valence of X and whereby X does not unduly interfere with the functioning of the molecule as a surfactant..

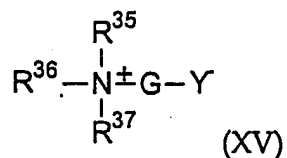
34. The method of Claim 29, wherein the surfactant comprises one or more cationic surfactants that may be a quaternary amine-based surfactant according to the structural formula XIV:



5 wherein:

each R^{31} , R^{32} , R^{33} , and R^{34} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen containing hydrocarbon radicals, and J is a suitable anion having a valence or
10 oxidation state p that does not unduly interfere with the functioning of the molecule as a surfactant.

35. The method of Claim 29, wherein the surfactant comprises one or more amphoteric surfactants according to the structural formula XV:



15 wherein:

each R^{35} , R^{36} and R^{37} is independently H or a monovalent hydrocarbon group of 1 to 30 carbons selected from the group consisting of linear, cyclic, and branched hydrocarbon radicals and linear, cyclic and branched chalcogen containing hydrocarbon radicals, G is a divalent spacer group, and Y is a
20 carboxylate, sulfonate, sulfate, phosphonate or other similar group.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 01/26918

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06L1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D06L C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|----------------------------------|
| X | EP 1 043 443 A (GEN ELECTRIC) 11 October 2000 (2000-10-11) page 4, line 2 - line 40; claim 8; example 3 --- | 1-24, 27, 29-34 |
| X | EP 1 041 189 A (GEN ELECTRIC) 4 October 2000 (2000-10-04) claim 1; example 2 --- | 1-4, 6, 28, 29 |
| X | DE 37 39 711 A (KREUSSLER CHEM FAB) 8 June 1989 (1989-06-08) page 3, line 1 - line 7; claim 2; example 2 --- | 1-6, 16, 20-23, 28, 29, 34 |
| X | US 6 063 135 A (BERNDT DIETER R ET AL) 16 May 2000 (2000-05-16) column 7, line 40 - line 56; claims 1, 2 --- -/-- | 1, 4-6, 28, 29 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

12 March 2002

Date of mailing of the international search report

27/03/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Saunders, T

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/26918

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|--|
| X | EP 0 458 969 A (TOKYO SHIBAURA ELECTRIC CO) 4 December 1991 (1991-12-04) | 1,5-8, 16-19, 27,29, 30,33 |
| A | examples 3-5 --- | 2,3 |
| P,X | EP 1 092 803 A (UNILEVER PLC; UNILEVER NV (NL)) 18 April 2001 (2001-04-18) | 1,4-8, 16, 20-25, 28-30, 33-35 |
| | page 3, line 27 - line 31; claims 7-12 --- | |
| E | WO 01 94684 A (PROCTER & GAMBLE) 13 December 2001 (2001-12-13) | 1,4-8, 20-23, 27-30,34 |
| | page 7, paragraph 5 -page 8, paragraph 1 page 20, paragraph 2 -page 23, paragraph 2; claims 7-12 --- | |
| A | DATABASE WPI Section Ch, Week 198201 Derwent Publications Ltd., London, GB; Class D25, AN 1982-00888E XP002192566 & JP 56 155299 A (LION CORP), 1 December 1981 (1981-12-01) abstract ----- | 1,4, 24-26, 29,35 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/26918

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| EP 1043443 | A | 11-10-2000 | US 6310029 B1 | 30-10-2001 |
| | | | EP 1043443 A1 | 11-10-2000 |
| | | | JP 2000313900 A | 14-11-2000 |
| | | | US 2001034912 A1 | 01-11-2001 |
| EP 1041189 | A | 04-10-2000 | EP 1041189 A1 | 04-10-2000 |
| | | | JP 2000319694 A | 21-11-2000 |
| DE 3739711 | A | 08-06-1989 | DE 3739711 A1 | 08-06-1989 |
| US 6063135 | A | 16-05-2000 | US 5942007 A | 24-08-1999 |
| | | | US 5865852 A | 02-02-1999 |
| | | | AU 4993599 A | 07-02-2000 |
| | | | AU 5101799 A | 07-02-2000 |
| | | | BR 9912088 A | 10-04-2001 |
| | | | BR 9912811 A | 02-05-2001 |
| | | | CN 1309733 T | 22-08-2001 |
| | | | CN 1309734 T | 22-08-2001 |
| | | | EP 1084289 A1 | 21-03-2001 |
| | | | EP 1092056 A1 | 18-04-2001 |
| | | | HU 0102648 A2 | 28-12-2001 |
| | | | NO 20010231 A | 14-03-2001 |
| | | | NO 20010232 A | 14-03-2001 |
| | | | WO 0004221 A1 | 27-01-2000 |
| | | | WO 0004222 A1 | 27-01-2000 |
| | | | US 6042617 A | 28-03-2000 |
| | | | US 6056789 A | 02-05-2000 |
| | | | US 6042618 A | 28-03-2000 |
| | | | US 6086635 A | 11-07-2000 |
| | | | US 6059845 A | 09-05-2000 |
| EP 0458969 | A | 04-12-1991 | DE 69031030 D1 | 14-08-1997 |
| | | | DE 69031030 T2 | 11-12-1997 |
| | | | EP 0458969 A1 | 04-12-1991 |
| | | | KR 9307226 B1 | 04-08-1993 |
| | | | RU 2104331 C1 | 10-02-1998 |
| | | | US 5977040 A | 02-11-1999 |
| | | | US 6136766 A | 24-10-2000 |
| | | | US 5443747 A | 22-08-1995 |
| | | | CA 2034488 A1 | 27-04-1991 |
| | | | CA 2151846 A1 | 27-04-1991 |
| | | | CA 2151847 A1 | 27-04-1991 |
| | | | CA 2151848 A1 | 27-04-1991 |
| | | | CA 2151849 A1 | 27-04-1991 |
| | | | CN 1095410 A ,B | 23-11-1994 |
| | | | CN 1103113 A ,B | 31-05-1995 |
| | | | EP 0673995 A2 | 27-09-1995 |
| | | | EP 0673996 A2 | 27-09-1995 |
| | | | HK 1001094 A1 | 22-05-1998 |
| | | | JP 2963406 B2 | 18-10-1999 |
| | | | JP 9176697 A | 08-07-1997 |
| | | | JP 2752352 B2 | 18-05-1998 |
| | | | JP 9188897 A | 22-07-1997 |
| | | | WO 9106621 A1 | 16-05-1991 |
| | | | JP 2949201 B2 | 13-09-1999 |
| | | | JP 7216569 A | 15-08-1995 |
| | | | JP 2656450 B2 | 24-09-1997 |
| | | | JP 7216387 A | 15-08-1995 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/26918

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP 0458969 | A | SG 47816 A1 | 17-04-1998 |
| | | SG 47130 A1 | 20-03-1998 |
| | | US 5728228 A | 17-03-1998 |
| | | US 5741365 A | 21-04-1998 |
| | | US 5985810 A | 16-11-1999 |
| | | US 5716456 A | 10-02-1998 |
| | | US 5741367 A | 21-04-1998 |
| | | CN 1051196 A ,B | 08-05-1991 |
| | | JP 2651453 B2 | 10-09-1997 |
| | | SG 47860 A1 | 17-04-1998 |
| EP 1092803 | A | 18-04-2001 | |
| | | US 6309425 B1 | 30-10-2001 |
| | | EP 1092803 A1 | 18-04-2001 |
| | | US 2002023305 A1 | 28-02-2002 |
| WO 0194684 | A | 13-12-2001 | |
| | | US 2002007519 A1 | 24-01-2002 |
| | | US 2001054202 A1 | 27-12-2001 |
| | | WO 0193977 A2 | 13-12-2001 |
| | | WO 0194684 A1 | 13-12-2001 |
| | | WO 0194501 A2 | 13-12-2001 |
| | | WO 0194682 A1 | 13-12-2001 |
| | | WO 0194679 A2 | 13-12-2001 |
| | | WO 0194686 A2 | 13-12-2001 |
| | | WO 0194675 A2 | 13-12-2001 |
| | | WO 0194685 A1 | 13-12-2001 |
| | | WO 0194521 A1 | 13-12-2001 |
| | | US 2002004950 A1 | 17-01-2002 |
| | | US 2002017493 A1 | 14-02-2002 |
| | | US 2002010964 A1 | 31-01-2002 |
| | | US 2002004995 A1 | 17-01-2002 |
| | | US 2002013234 A1 | 31-01-2002 |
| | | US 2002004952 A1 | 17-01-2002 |
| | | WO 0194683 A1 | 13-12-2001 |
| | | WO 0194678 A1 | 13-12-2001 |
| | | WO 0194681 A1 | 13-12-2001 |
| JP 56155299 | A | 01-12-1981 | |
| | | JP 1337061 C | 11-09-1986 |
| | | JP 61002117 B | 22-01-1986 |

THIS PAGE BLANK (USPTO)